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A method of manufacturing elastic moulded components, in particular vehicle tyres, by casting

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The invention relates to a method of manufacturing elastic moulded elements, in particular motor vehicle tyres, by casting.

When manufacturing elastic moulded elements, such as tyres, buffers, rubber spring components, using standard rubber mixtures, a considerable amount of effort is generally required in order to produce the blank and obtain a finished moulded element exhibiting the various properties that will be required of different components. Particularly in the case of tyres, various proposals have therefore been put forward as a means of making the tyre body by casting using plastics. To this end, a liquid reaction mixture is used which is subsequently cured by cross-linking.

However, tyres and similar moulded objects subjected to a high degree of stress made from resilient plastics of this type, e.g. polyurethane, have not proved to be totally satisfactory since the properties do not meet the demands placed on them in their different fields of application. The requirements for a tyre, for example, are a high resistance to slipping on its running surface, a relatively low build-up of heat during service, elastic behaviour conducive to good driving properties during running and a high mileage performance. These requirements

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place such high demands on the structure of the plastics which might be used for this application that as a rule that they can not be met to a sufficiently high degree on a large scale. In the context of the objective underlying the invention, therefore, it is important, starting with a liquid reaction compound at the outset, to be able to produce components which are capable of meeting the desired requirements placed on them in terms of their properties.

Surprisingly, the invention has achieved this objective due to the fact that a liquid compound of the composition below essentially reaches transformation point when heated to 100 to 180°. The constituents of this compound, denoted by A, B, C, are as follows:

A) polybutadiene and/or polyisoprene and other equivalents having a molecular weight of 2000 to 20000 and terminal carboxyl and/or hydroxyl groups.

B) bis-cyclohexene oxides, in which the cyclohexane rings are linked to one another by means of an ester chain.

C) 1,2-dicarboxylic acid anhydride of cyclohexane and/or cyclohexene.

In these compounds, for every 1 equivalent proportion of A, 2 to 20 equivalent proportions of B and C are used, it being preferable if B and C differ by two equivalent proportions at most.

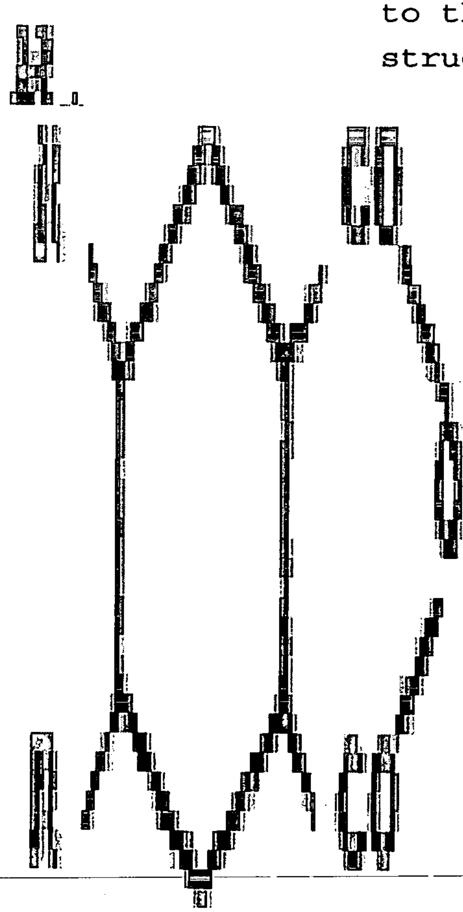
The equivalent proportion A relates to the carboxyl or hydroxyl groups, the equivalent proportion B to the epoxy groups and the equivalent proportion C to the anhydride groups. As appropriate, polydienes falling under category A may also include polymers of demethylated butadiene, piperylene or chloroprene incorporating carboxyl or hydroxyl groups, provided they have a low molecular weight and are liquid at room temperature. Furthermore, the liquid polymers A of the above-mentioned dienes may also be copolymers with up to 30% styrene, acrylonitrile, acrylic acid ester, fumaric acid ester etc.. Saturated polyesters and polyethers may also be considered for the system A, B, C provided they can be combined to produce the desired profile of properties. However, butadienes carrying carboxyl or hydroxyl terminal groups are preferred in this application.

As a result of the capacity for variation within said limits, it is possible on the one hand to lengthen the chain and on the other to produce cross-linking to obtain a very well controlled structure, the dicarboxylic acid anhydride having the effect of allowing increased effective control as regards the flexibility of the chains. This can be even be further enhanced if mono-epoxide substances are used in addition. Examples are styrene oxide, cyclohexene oxide, phenoxy-propene oxide. Accordingly, provided the limits for the equivalent proportions are complied with, improved flexibility will be achieved with higher insensitivity to temperature. Components B and C can be regarded as the resin element. If used in optimum proportions, they will have a significant enhancing effect in terms of strength and abrasion so that the addition of strengthening fillers such as carbon black can be dispensed with under certain

circumstances. /4
Furthermore, the resin element can be used to regulate the stiffness of the cured material such that it can be used to manufacture tyres without any fabric or layers of cord.

The dicarboxylic acid anhydrides used for C can be readily obtained by diene synthesis by means of a Diels-Alder reaction followed by hydration. The epoxides can also be obtained relatively easily by a Diels-Alder reaction followed by epoxidation and the end-product can be produced on an economically viable scale.

With regard to the bis-cyclohexene oxides used as component B, reference may be made to the following chemical structures:



General formula:

R1-R6- = H or methyl-

Examples for -X- =

-CH2-O-CO-
-CH2-O-CO-(CH2)2-CO-O-CH2-
-CH2-O-CO-(CH2)4-CO-O-CH2-
-CO-O-(CH2)2-O-CO-
-O-CO-(CH2)2-CO-O-
-CH2-O-CO-CH=CH-CO-O-CH2-

Examples for component C are

R = H or methyl-

The compounds can be processed using rotary or centrifugal casting moulds so that a layered structure can be built up. This being the case, the requisite characteristic properties can be imparted to the layers by metering the components A to C accordingly. If higher molecular weights relative to that of compound A are used to produce the casting compound, the number of equivalent proportions relative to B and C should be in the upper threshold range. With a butadiene of molecular weight of 12000, approximately 8 to 10 equivalents of B and C will be used. Apart from carboxide and hydroxyl groups, other terminal groups may also be used, e.g. mercaptan, provided the related secondary effects are not incompatible with the application. However, it is preferable to use the specified carboxyl and hydroxyl groups.

The transformation of components A to C can be accelerated by using additives that are known per se. These include, for example, tertiary amines, heterocyclic amines and quarternary ammonium salts. It is also possible to use salts or complex salts of metals of varying valency such as nickel, chromium, tin and iron. The known accelerators used for epoxides only can also be used without detriment to the transformation process outlined above. Alkylated phenols, bisphenols and/or secondary aromatic amines and diamines may also be added in order to increase the resistance to ageing.

For specific ranges, the material can also be made stiffer in a specified direction by incorporating fibres of glass, steel, polyester, polyamide or rayon with the still fluid reaction compound.

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The cut-length is approximately 1 to 3 mm and the added quantity between 5 and 20% relative to the proportion of polybutadiene in the reaction compound. Although a considerable abrasion strength can be produced without using carbon black, it is nevertheless possible to add active or inactive fillers. The largely transparent compound may be coloured using dyes of the required colour in pigment form.

Example 1

The starting materials are as follows:

A) Liquid polybutadiene with carboxyl terminal groups and an average degree of polymerisation of 90. The equivalent weight (calculated on the basis of the titrated carboxyl value) is 2380.

B) Expoxycyclohexyl-methyl ester of expoxycyclohexane carboxylic acid. The equivalent weight (calculated on the basis of the titrated epoxide value) is 140.5.

C) 4-methyl-cyclohexane-dicarboxylic acid anhydride. Equivalent weight: 168 (calculated on the basis of the titrated acid number A, B, C).

Equivalent ratio: 1/5/4 for the following mix.

Polybutadiene (A)	100 g
Bis-cyclohexene oxide (B)	30 g
Anhydride (C)	28 g

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The three liquid proportions of constituent elements - at room temperature - are thoroughly mixed in a rotary evaporator for 15' at 80°C by means of slow rotation, a slight vacuum being applied for a brief period to remove air bubbles. 1 ml of butyl-imidazol is then added as a curing catalyst and mixed for a further 5'. The casting compound is then poured into a sheet-iron plate mould (135 x 155 mm) sprayed with Teflon (polytetrafluoroethylene), having inclined walls and cured in the drying cabinet for 4 hours at 100°. The 8 - 9 mm thick plate is broken up into 2 mm and 6 mm pieces and the sample pieces required for measuring the physical properties punched or cut out. The cured material has a specific weight of 1.01 g/cm^3. The benzene extract was 3.0%, which implies that the constituent elements are almost completely set. The volume expansion in driving petrol: 120%.

The tests to obtain mechanical data produced the following values:

Breaking strength:	140 kg/cm^2
Elongation at break:	150%
Shore hardness (A):	85
Rebound elasticity:	45%
Friction (per DIN 53516):	190

During flexing endurance testing, 2 mm thick and 25 mm wide strips still resisted breaking and exhibited no tearing in the De Mattia machine after 500 kilocycles.

This casting compound is suitable for producing a cord-free carcass in a moulded tyre since it has the requisite stiffness whilst retaining flexing capability.

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Example 2

The same starting materials as those of example 1, but in a different ratio of equivalents (1/6/4)

Polybutadiene (A)	100 g
Bis-cyclohexene oxide (B)	35.5 g
Anhydride (C)	28 g
Butyl-imidazol	1 g

As in example 1, the constituent elements were mixed by rotation at 80°C and the thoroughly mixed compound poured into a plate mould and left to set for 15' at 140°C and then heated for 2 hours at 100°C

Benzene extract:	4.3%
Shore hardness A:	62
Residual set at 70°C per DIN:	17%

Example 3:

A different bis-cyclohexene oxide (B2) is used in this example, namely epoxy cyclohexyl-methyl diester of adipic acid (equivalent weight: 212.5).
Equivalent ratio (A/B/C) = 1/5/4.

Polybutadiene (A 1)	100
Bis-cyclohexene oxide (B 2)	45
Anhydride (C 1)	28
Butyl-imidazol	1
Chrome-III-diisopropylsalicylate	0.5

Mixed as in examples 1 and 2.
Curing: heated 20'/140° + 4 hours/100°.

Breaking strength:	114 kg/cm^2
Elongation at break:	200%
Modulus at 100% expansion	52 kg/cm^2
Shore hardness A	89
Rebound elasticity	36%
Tear propagation per Graves	16 kg/cm
Benzene extract	3.8%
Specific weight	1.01 g/cm^3

<u>Example 4</u>

	a)	b)
Polybutadiene (A 1)	100	100
Bis-cyclohexene oxide (B 1)	24	24
Anhydride (C 1)	21	21
2,2'-methylene-bis-(4-methyl-6-tert.-butyl-phenol) (Anti-ageing agent BKF made by Farbenfabriken Bayer)	0.5	-
N-Phenyl-N'-isopropyl-p-phenylene diamine (Anti-ageing agent 4010 NA made by Farbenfabriken Bayer)	1	-
Butyl imidazol	1	1
Tin octoate	0.25	0.25

Equivalent ratio: 1/4/3
Curing: 10'/140° (a), 15'/140° (b), then heated for 2 hours at 100°C.

Strips 2 mm thick and 25 mm wide were prepared from the plates and these were tested in the ozone cabinet at 200 pphm ozone and at room temperature in a severely bent state.

Sample 6 had already completely broken after 6 hours whilst sample a exhibited neither breaking nor tearing after 48 hours. This test provides evidence that the standard, highly-effective anti-ageing agents normally used with natural and synthetic rubber are also effective with this rubber system. They are not rendered ineffective by the other elements in the mixture and do not disrupt the curing process but in fact tend to accelerate it slightly.

Example 5

Two different pre-polymers were used in this example, namely:

A2 a liquid copolymer of butadiene and acrylonitrile (20% acrylonitrile content with carboxyl terminal groups.
Mean degree of polymerisation: 60
(calculated from the acid number)
Equivalent weight: 1920

A3 a copolymer of butadiene and acrylonitrile (15% acrylonitrile content) with hydroxyl terminal groups.
Mean degree of polymerisation:
(calculated on the basis
of the hydroxyl number) 83
Equivalent weight: 1670

Mixtures

	a)	b)	c)	d)
Equivalent ratio (A/B/C)	1/4/3.4	1/5.5/4.5	1/3.5/3.0	1/4.8/4.0
Polybutadiene-acrylonitrile (A2)	100	100	-	-
Polybutadiene-acrylonitrile (A3)	-	-	100	100
Biscyclohexene oxide (B1)	30	40	30	40
Anhydride (C1)	30	40	30	40
Butyl-imidazol	1	1	1	1
Chrome(III)-diisopropylsalicylate	0.25	0.25	0.25	0.25
Curing	------10' / 150° C --------------------			
Subsequent heating	------2 hours / 100° C ----------------			
Specific weight	1.05	1.06	1.04	1.05
Breaking strength (kg/cm²)	131	142	107	136
Elongation at break	140	100	160	110
Shore hardness A	89	95	68	84
Rebound elasticity (%)				
at 20°C	29	42	24	26
at 100°C	35	32	49	40
Shear modulus = 1000 kg/cm² and torsion test device per Schmieder-Wolf at °C	- 6°	+ 20°	- 20°	- 10°
Benzene extract (%)	2.4	1.6	8.5	6.1

This material is suitable for the manufacture of moulded rubber articles resistant to fuel, oil and fat.

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Example 6

Polybutadiene (A 1)	100
Bis-cyclohexene oxide	30
Cyclohexene-dicarboxylic acid-anhydride (Diels-Alder adduct from butadiene and maleic acid anhydride) (C2)	26
Dimethylbenzylamine	2

Equivalent ratio: 1/5/4

Cured 15′ at 140° and heated for 4 hours at 70°.

Specific weight: 1.02

Breaking strength: 74 kg/cm²

Elongation at break: 140%

Modulus at 100% expansion 52 kg/cm²

This mixture must be mixed at 100°C since the anhydride C2 is solid and does not melt until about 100°.

Example 7

	a)	b)
Polybutadiene (A 1)	100	100
Bis-cyclohexene oxide (B 1)	24	24
Phenoxy-propenoxide (D 1)	6	-
Styrene oxide (D 2)	-	5
Anhydride (C 1)	28	28
Cetyl-trimethyl ammonium bromide	1	1

	a)	b)
Equivalent ratio (A/B/D/C)	1/4/1/4	1/4/1/4

Curing: 4 hours at 100°C

	a)	b)
Specific weight	1.01	1.01
Breaking strength	84 kg/cm²	114
Elongation at break	180%	180
Modulus (200%)	53	55
Tearing propagation per Graves	9 kg/cm	10

Shore hardness A	84	88
Rebound elasticity	30%	39

Example 8

Polybutadiene (A 1)	100	100
Bis-cyclohexene oxide (B 1)	24	24
Anhydride (C 1)	21	21
Butyl imidazol	1	1
Cut glass fibre (3 mm)	8	-
Cut polyester fibre (2 mm)	-	5

The above constituent elements were mixed by slow rotation in a rotary evaporator under vacuum at 80°C. The cut fibres were uniformly distributed in the compound free of air. The plates - cured 15'/140°C - exhibited a significantly increased stiffness, particularly the plate with the glass fibre.

Example 9

The following two examples are intended to demonstrate that the claimed "anhydride system" can also be used on pre-polymers other than polydienes.

Polyethylene adipate Hydroxyl-terminated (Equivalent weight ≈ 1000)	100	-
Polypropylene oxide hydroxyl-terminated (Equivalent weight ≈ 1000)	-	100
Bis-cyclohexene oxide (B 1)	56	56
Anhydride	50	50
Butyl imidazol	1	1
Tin octoate	0.25	0.25

Shore hardness A	84	88
Rebound elasticity	30%	39

Example 8

Polybutadiene (A 1)	100	100
Bis-cyclohexene oxide (B 1)	24	24
Anhydride (C 1)	21	21
Butyl imidazol	1	1
Cut glass fibre (3 mm)	8	-
Cut polyester fibre(2 mm)	-	5

The above constituent elements were mixed by slow rotation in a rotary evaporator under vacuum at 80°C. The cut fibres were uniformly distributed in the compound free of air. The plates - cured 15'/140°C - exhibited a significantly increased stiffness, particularly the plate with the glass fibre.

Example 9

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Polyethylene adipate Hydroxyl-terminated (Equivalent weight ≈ 1000)	100	-
Polypropylene oxide hydroxyl-terminated (Equivalent weight ≈ 1000)	-	100
Bis-cyclohexene oxide (B 1)	56	56
Anhydride	50	50
Butyl imidazol	1	1
Tin octoate	0.25	0.25

Equivalent ratio 1/4/3 1/4/3

Curing: 15' / 140°C

Subsequent heating: 12 hours/80°C. /14

Equivalent ratio	1/4/3	1/4/3

Curing: 15′ / 140°C

Subsequent heating: 12 hours/80°C. /14

Specific weight	1.22	1.11
Breaking strength (kg/cm^2)	67	39
Elongation at break (%)	130	120
Modulus (100%) (kg/cm^2)	47	31
Shore hardness A	76	74
Rebound elasticity		
at 20°C	13	14
at 100°C	45	32

Claims

1. A method of producing elastic moulded components, in particular motor vehicle tyres, by casting, characterised in that liquid compounds of the following composition are brought to transformation by heating to 100 - 180°C

polybutadiene and/or polyisoprene and other similar substances with a molecular weight of 2000 to 20000 and terminal carboxyl and/or hydroxyl groups or optionally mercaptan groups,

B) bis-cyclohexene oxide, in which the cyclohexane ranges are linked to one another by an ester chain,

C) dicarboxylic acid anhydride of cyclohexane and/or cyclohexene

and in which to every equivalent A, 2 to 20 equivalents of B and C are added and the equivalent of B differs from the equivalent of C by at most 2 equivalents and the equivalent of A is relative to carboxyl or hydroxyl groups, the equivalent of B to epoxide groups and the equivalent of C to anhydride groups.

2. A method as claimed in claim 1, characterised in that if A is of higher molecular weights, the number of equivalents of B and C is in the upper threshold limit and at lower molecular weights in the lower threshold range.

3. A method as claimed in claims 1 and 2, characterised in that mono-epoxides are also added to the reaction compound.

4. A method as claimed in claims 1 to 3, characterised in that the compound is transformed in the presence of tertiary amines, heterocyclic amines or quaternary ammonium salts and optionally also salts or complex compounds of metals of varying valency.

5. A method as claimed in claims 1 to 4, characterised in that alkylated phenols, bisphenols and/or secondary aromatic amines and/or N,M'-p-phenylene diamine derivatives are added to the compound.

6. A method as claimed in claims 1 to 5, characterised in that cut fibres of glass, steel, polyester, polyamide, rayon, cellulose are added to the compound.

7. A method as claimed in claims 1 to 6, characterised in that fillers, dyes are added to the compound.